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Radiolysis of Paraffin Encapsulation Wax

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파라핀 고화체의 방사선적 가수분해

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Abstract—An estimate is made on the potential generation rate of H_2 from radiolysis of the paraffin-wax encapsulant proposed for the solidified liquid concentrate wasteform. The results show that the radiolytic production of H_2 from paraffin-wax-encapsulated waste is dominated by the radiation energy released from ^{60}Co. The radiolytic production of H_2 will proceed at an initial rate equivalent to aproximately 4.4×10^{-2} cm^3yr^{-1} in 200 litre drums that are partly filled with 120 litres of encapsulated waste. The gas production rate will fall to a value of $7.2cm^3yr^{-1}$ after 100 years. The lower flammable limit for H_2 in air will be reached in about 25 years and the lower explosive limit for H_2 in air would not be reached in 1000 years. The timescale in which these safety-related limits are reached is strongly dependent on the level of filling of each waste drum. A reduction of the air space inside each drum would reduce the time required to reach the lower flammable limit.

Key words : radiolysis, paraffin wax, radioactive waste, gas generation, G value, flammable limit, explosive limit

요약—파라핀 왁스를 사용하여 건조된 농축폐액을 고화시킬 경우, 방사선적 가수분해에 의해 발생할 가능성이 있는 수소가스의 발생량을 추정하여 보았다. 분석결과에 의하면, 코발트 60의 방사선 에너지에 의해 방사선적 가수분해가 주로 발생함을 알 수 있다. 200리터 드럼중 120 리터가 파라핀으로 채워졌다고 가정할 때 수소가스 발생은 초기에 4.4×10^{-2} cm^3yr^{-1} 이고 100년이 경과한 후는 $7.2cm^3yr^{-1}$로 줄어든다. 수소에 의한 발화점을 25년이 경과한 후 도달할 가능성이 있으나, 폭발한계에는 1000년 이내에 도달할 가능성이 없다. 안전성 관련 주요 한계점에 도달하는 시기는 드럼내 파라핀 왁스의 채움 정도에 매우 민감하게 영향을 받는다. 드럼내 공간의 감소시, 발화점에 도달 시간이 줄어듬을 알 수 있다.

중심단어 : 가수분해, 파라핀고화체, 방사성폐기물, 가스생성, G값, 발화점, 폭발점

INTRODUCTION

In this paper, an estimate is made on the potential generation rate of H_2 from radiolysis of the paraffin-wax encapsulant proposed for the solidified liquid concentrate wasteform.

One potential Korean radioactive waste stream involves the use of paraffin wax as an encapsulant for solidified liquid concentrate. There is a question as to the amount of radiolytic H_2 that could be produced by the action of ionizing radiation on the paraffin encapsulant. Although the generation rate of H_2 from this source is not likely to be significant in comparison to that from anaerobic corrosion of steel packaging and waste, there may be implications for the wasteforms themselves, for example with regard to flammability and explosion hazards. This paper addresses this particular issue.

ENERGY ABSORPTION

Assessment of energy absorption rate

In this analysis, it is assumed that 10,000 drums of paraffin-wax-based waste is to be disposed of in the proposed underground repository for low-level radioactive waste. An initial step is to summarize and tabulate the total radiation energy absorbed by the paraffin wax. Energies and emission types used in this table are taken from reference[1].

A summary of all the relevant data at the time of repository closure is given in Table 1. It can be seen that the energy term is dominated by ^{60}Co (for gamma emission).

Correction for escaping gamma emissions

The ^{60}Co emissions are gammas and so have a considerably greater range than any of the other emissions. A significant amount of the radiation energy may escape from the waste drum and therefore, for the purposes of this calculation, must be discounted.

To quantify this it is assumed (as an approximation) that all the activity is located on the center line of the drum and has to pass through a thickness, t, of paraffin wax equivalent to the radius of the drum, taken to be 25cm. The average gamma energy is 1.25 MeV and the linear attenuation coefficient, μ, for 1 MeV photons in paraffin is $0.0646cm^{-1}$[2].

Thus,

$$I=I_0e^{-\mu t}, \qquad (1)$$

where I/I_0 is the fraction of the gamma photons emerging from the paraffin wax, and μ and t are $0.0646cm^{-1}$ and 25cm respectively. Consequently, $I/I_0=0.199$. It follows that the energy absorption rate of Co-60 from the emission rate of $8.324\times10^{13}s^{-1}$ with the average gamma energy of 1.25 MeV is

$$(1-I/I_0)\times8.324\times10^{13}s^{-1}\times1.25Mev$$
$$=8.332\times10^{13}\ MeV\ s^{-1}.$$

It is possible (depending on how the drums are grouped in the repository cavern) that some of the gamma energy escaping from one drum may be absorbed in a neighbouring drum. That possibility is not included in this assessment.

Correction for self-absorption of alpha radiation emissions

Alpha radiation emissions are of very limited range; in practice the alpha radiation source is not disposed as discrete atoms, but as particles that are prone to absorb the emitted radiation energy from the decaying atoms within each particle [3]. The consequent radiation levels to the paraffin wax are dependent upon the particle size and the degree of self-absorption. This is a complex subject. In the present assessment it is assumed that ^{238}U will be present as particulate of uniform size, either >12 μm or 1μm radius.

From reference 3, it is estimated that the energy self-absorption by U particles of radius >12μm will reduce the effective emission to 7.74×10^{1} MeV s^{-1}. This represents a very

significant reduction from the energy emission rate (3.54×10^{7} MeV s^{-1}) given in Table 1. Si mply, it means that no matter how much U is present, if most of the emission energy is self-absorbed then the amount of energy emitted to the paraffin wax is bounded by an upper limit determined by the particle size and the range of alpha radiation in UO_2. However, if the UO_2 particles are of radius 1μm, then self-shielding is minimal and virtually the full potential emission to the paraffin wax is realized (3.54×10^{7} MeV s^{-1} for ^{238}U).

This assessment is therefore extremely se nsitive to the assumed particle size. The overall effect of increasing particle size is to reduce the impact of alpha radiolysis to that of a minor influence, over the repository lifetime.

Summary of energy absorption rate

The total energy absorption is dominated by the term representing the ^{60}Co emissions (88% of the total, with ^{137}Cs contributing 10%). Since the ^{60}Co emissions are gammas, the absorbed energy will be evenly distributed within the wasteform. For this assessment, the two emission types will almost entirely describe the radiolysis of paraffin wax in this disposal situation.

ASSESSMENT OF RADIOLYTIC GAS PRODUCTION

G-value data

The yields of gaseous radiolysis products will depend on the G values (number of molecules

Table 1. Paraffin wax inventory at time of repository closure

Radionuclide	Half-life(year)	Activity[a] (Bq)	Energy (MeV) (emission Type)	Energy absorption rate (MeV s^{-1})
^{3}H	1.23×10^{1}	2.547×10^{12}	0.018(β)	4.585×10^{10}
^{14}C	5.57×10^{3}	1.463×10^{12}	0.158(β)	2.311×10^{11}
^{60}Co	5.30×10^{0}	8.324×10^{13}	1.173, 1.332(γ)[b]	(1.041×10^{14})[c]
				8.332×10^{13}
^{59}Ni	1.00×10^{5}	4.257×10^{12}	0.002, 0.004(γ,β)	2.554×10^{10}
^{63}Ni	1.20×10^{2}	4.997×10^{12}	0.067(β)	3.348×10^{11}
^{90}Sr	2.80×10^{1}	2.414×10^{11}	0.540(β)	1.303×10^{11}
^{94}Nb	2.00×10^{4}	1.539×10^{11}	1.571, 0.001(γ,β)	2.419×10^{11}
^{99}Tc	2.10×10^{5}	2.091×10^{11}	0.300(β)	6.273×10^{10}
^{129}I	1.60×10^{7}	9.692×10^{9}	0.150(β)	1.454×10^{9}
^{137}Cs	3.00×10^{1}	1.804×10^{13}	0.510(β)	9.200×10^{12}
^{238}U	4.50×10^{9}	8.438×10^{6}	4.190(α)	(3.535×10^{7})[d]
				7.74×10^{1}
Total	–	1.152×10^{14}	–	9.359×10^{13}

(a) Assumed activity in 10,000 drums encapsulated by paraffin wax.
(b) Range of γ-activity for ^{60}Co (mean value is 1.25 MeV).
(c) See Correction for escaping gamma emmissions; the value in brackets is the maximum absorption rate, the value without brackets is the calculated rate taking into account energy loss due to gamma range.
(d) See Correction for self-absorption of alpha radiation emmissions; the value in brackets is the maximum absorption rate assuming a particle size of about 1 μm radius; the value without brackets is calculated rate assuming particle sizes of > 12 μm radius taking into account energy self-absorption in the particles.

produced per 100 eV of absorbed energy) for the alpha and gamma radiations (note that these values are dependent on the radiation type).

G-value data for the production of gaseous products are not directly available for paraffin wax; analogies must be drawn from chemically similar compounds. For ^{60}Co gamma irradiation of n-hexadecane (a paraffin which is approaching the soild state (wax) at room temperature, melting point 4℃) a G value of 4.0 has been measured for hydrogen production from the paraffin in the solid state [4]. This value will be used as representative for the paraffin wax used as an encapsulant, and is also assumed to be relevant to beta radiolysis from the ^{137}Cs present.

However, there is little comparable data for alpha particle radiolysis of paraffins; it is generally acknowledged that, for comparable systems (such as cyclohexane), alpha radiolysis will produce hydrogen with a G value of between 4 and 5 [5], and thus an average value of 4.5 could be used. For comparison, alpha radiolysis of polyethylene gives a $G(H_2)$ between 2.7 and 3.7, depending on temperature [6], whereas gamma radiolysis of polyethylene gives a $G(H_2)$ of between 3 and 5 [7] (depending on molecular weight, a parameter which was not addressed in reference [6], and also with temperature).

Yield calculation

The absorbed energy total is for 10,000

Table 2. Paraffin wax inventory after 100 years.

Note : Adjustments over the 100-year time scale have only been made to those isotopes with half-lives less than 5000 years (cf. Table 1)

Radionuclide	Half-life (year)	Activity (Bq)	Energy (MeV) (emission Type)	Energy absorption rate (MeV s^{-1})
^{3}H	1.23×10^{1}	9.091×10^{9}	0.018(β)	1.636×10^{8}
^{14}C	5.57×10^{3}	1.463×10^{12}	0.158(β)	2.311×10^{11}
^{60}Co	5.30×10^{0}	1.739×10^{8}	1.173-1.332(γ)[a]	(2.17×10^{8})[b] 1.75×10^{8}
^{59}Ni	1.00×10^{5}	4.257×10^{12}	0.002, 0.004(γ,β)	2.554×10^{10}
^{63}Ni	1.20×10^{2}	2.804×10^{12}	0.067(β)	1.878×10^{11}
^{90}Sr	2.80×10^{1}	2.030×10^{10}	0.540(β)	1.096×10^{10}
^{94}Nb	2.00×10^{4}	1.539×10^{11}	1.571, 0.001(γ,β)	2.419×10^{11}
^{99}Tc	2.10×10^{5}	2.091×10^{11}	0.300(β)	6.273×10^{10}
^{129}I	1.60×10^{7}	9.692×10^{9}	0.150(β)	1.454×10^{9}
^{137}Cs	3.00×10^{1}	1.517×10^{12}	0.510(β)	7.736×10^{11}
^{238}U	4.50×10^{9}	8.438×10^{6}	4.190(α)	(3.535×10^{7})[c] 7.74×10^{1}
Total	–	1.044×10^{13}	–	1.535×10^{12}

(a) Range of γ-activity for ^{60}Co (mean value is 1.25 MeV).

(b) See Correction for escaping gamma emmissions; the value in brackets is the maximum absorption rate, the value without brackets is the calculated rate taking into account energy loss due to gamma range

(c) See Correction for self-absorption of alpha radiation emmissions; the value in brackets is the maximum absorption rate assuming a particle size of about 1 μm radius; the value without brackets is calculated rate assuming particle sizes of > 12 μm radius taking into account energy self absorption in the particles.

drums of paraffin wax. For each single drum (at the time of closure), the total energy absorbed will be 9.36×10^{9} MeV s^{-1}. In each 200-litre drum there will be 120 litres of paraffin wax and 80 litres of air space.

Therefore, in each drum, the gaseous hydrogen production rate from beta/gamma radiolysis will be 9.36×10^{13}(100s of eV s^{-1})$\times$4.0 (G value)$=3.74\times10^{14}$ molecules s^{-1} (or $6.22\ 10^{-10}$ mol s^{-1}). This is equivalent to 1.96×10^{-2} mol yr^{-1}, or 4.4×10^{2} cm^3(STP)yr^{-1}.

However, as this is dominated by ^{60}Co, the rate will decrease in line with the half-life of ^{60}Co. After 100 years, the inventory will be as given in Table 2. The total beta/gamma emissions will be approximately 1.53×10^{12}MeV s^{-1} for the total inventory, or 1.53×10^{8} MeV s^{-1} per drum. This corresponds to a H_2 gas generation rate of approximately 7.2cm^3(STP)yr^{-1}.

The alpha radiolysis production rate of H_2 will be dependent on the particle size of the actinide species present. Two possible situations are considered, one where a particle of radius greater than 12μm gives a reduction in the effective alpha radiation dose rate due to self-shielding, and one where a particle of radius 1 μm allows nearly all the radiation energy to be deposited in the paraffin wax.

For the situation with the 12 μm particle radius, in each drum the rate of H_2 production will be 7.74×10^{1}(100s of eV s^{-1})$\times$4.5 (G value)$=3.5\times10^{2}$ molecules s^{-1}(or 5.8×10^{-22} mol s^{-1}). This is equivalent to 1.8×10^{-14} mol yr^{-1}, or $4.1\times10^{-10}$$cm^3(STP)yr^{-1}$. This production rate is negligible in comparison with the beta /gamma radiolytic H_2 production rate at both the outset and at 100 years.

For the situation with the 1μm particle radius, the rate of H_2 production will be 3.5×10^{7}(100s of eV s^{-1})$\times$4.5(G value)$=1.6\times10^{8}$ molecules s^{-1}(or 2.6×10^{-16} mol s^{-1}). This will be equivalent to 8.3×10^{-9} mol yr^{-1}, or 1.9×10^{-4} cm^3(STP)yr^{-1}. This production rate is again insignificant compared with the beta/gamma radiolytic production at both the outset and at 100 years.

Container gas changes

Initially, the total H_2 production rate in each 200-litre drum is approximately $4.4\times10^{2}cm^3$ yr^{-1}. This will mix with the existing air in the drum (80 litres) assuming that the drum has a gas-tight seal. The dominant radiation source (^{60}Co)has a half-life of 5.3 years, and so the radiolytic H_2 production rate will decrease significantly over the first 100 years (also decreasing will be the minor contributor ^{137}Cs, with a half-life of 30 years). It follows that significant limits will be reached as follows :

(a) The lower flammable limit for hydrogen in air (5% by volume) requires $4\times10^{3}cm^3$ of hydrogen per drum. Over the timescale required to produce this much hydrogen, the production rate will decrease significantly as the ^{60}Co will go through a number of half-lives; it is estimated (see Table 3) that the timescale to reach this hydrogen concentration will be of the order of 25 years.

(b) The lower explosive limit for hydrogen in air (15% by volume) requires $1.2\times10^{4}cm^3$ of H_2 per drum. This requires an additional 8×10^{3} cm^3 beyond the lower flam mable limit. From Table 3 it can be seen that at 100 years some 5.1×10^{3} cm^3 of H_2 per drum is produced. Beyond that time the rate will fall to a steady value about 4 cm^3yr^{-1} in a further 100 years; at 200 $\times$years the total production will be less than 6×10^{3} cm^3. Beyond that the production rate will be relatively steady, but over the following 800 years only some 3.2×10^{3} cm^3 will be produced and the drum atmosphere will therefore not approach the explosive limit over a 10^{3}-year timescale.

(c) Significant pressurization of the drum (i.e. pressures above 1.5 bar, which effectively make the drum a pressure vessel) requires 4.0×10^{4} cm^3 of H_2. This would require in excess of 10^{3} years, beyond which the in-

Table 3. Approximate rate of hydrogen gas production from paraffin wax waste

Time (years)	^{60}Co energy absorption total ($MeVs^{-1}$)	^{137}Cs energy absorption total ($MeV\ s^{-1}$)	Hydrogen generation rate (cm^3day^{-1})	Hydrogen generation rate (cm^3yr^{-1})	Cumulative hydrogen production (cm^3)
0	8.33×10^{13}	9.20×10^{12}	1.24	453.23	0
1	7.31×10^{13}	8.98×10^{12}	1.10	402.10	453
2	6.42×10^{13}	8.76×10^{12}	0.98	357.14	855
3	5.63×10^{13}	8.54×10^{12}	0.87	317.58	1212
4	4.94×10^{13}	8.33×10^{12}	0.77	282.76	1530
5	4.34×10^{13}	8.13×10^{12}	0.69	252.11	1812
6	3.80×10^{13}	7.93×10^{12}	0.62	225.12	2064
7	3.34×10^{13}	7.74×10^{12}	0.55	201.34	2290
8	2.93×10^{13}	7.55×10^{12}	0.49	180.39	2491
9	2.57×10^{13}	7.36×10^{12}	0.44	161.91	2671
10	2.25×10^{13}	7.18×10^{12}	0.40	145.60	2833
12	1.74×10^{13}	6.84×10^{12}	0.32	118.50	3110
14	1.34×10^{13}	6.51×10^{12}	0.27	97.32	3336
16	1.03×10^{13}	6.19×10^{12}	0.22	80.72	3522
18	7.92×10^{12}	5.89×10^{12}	0.19	67.66	3676
20	6.10×10^{12}	5.61×10^{12}	0.16	57.34	3806
22	4.69×10^{12}	5.34×10^{12}	0.13	49.14	3916
24	3.61×10^{12}	5.08×10^{12}	0.12	42.59	4011
26	2.78×10^{12}	4.83×10^{12}	0.10	37.31	4094
28	2.14×10^{12}	4.60×10^{12}	0.09	33.03	4166
30	1.65×10^{12}	4.38×10^{12}	0.08	29.53	4230
35	8.58×10^{11}	3.87×10^{12}	0.06	23.16	4365
40	4.46×10^{11}	3.42×10^{12}	0.05	18.93	4472
45	2.32×10^{11}	3.02×10^{12}	0.04	15.94	4561
50	1.21×10^{11}	2.67×10^{12}	0.04	13.67	4636
60	3.27×10^{10}	2.08×10^{12}	0.03	10.37	4757
70	8.83×10^{9}	1.63×10^{12}	0.02	7.2	4851
80	2.39×10^{9}	1.27×10^{12}	0.02	7.2	4923
90	6.46×10^{8}	9.92×10^{11}	0.02	7.2	4995
100	1.75×10^{8}	7.74×10^{11}	0.02	7.2	5067

This Table makes the approximation that the production of hydrogen is dominated by ^{60}Co and ^{137}Cs and the decrease in gas production rate between time 0 and 55 years is only due to their decay. Between 70 and 100 years the production rate is taken to be constant at 7.2 cm^3yr^{-1} as calculated from the total inventory derived in Table 2.

tegrity of the drum may not, in any case, be certain.

It should be noted, however, that these timescales are strongly dependent upon the volume of each drum that is filled with waste. If, for example, each drum contained not 120 but 160 litres of encapsulated wastes, then the timescales to reach the relevant limits would be significantly reduced as follows: to reach lower flammable limit— approximately 6 years; to reach lower explosive limit—approximately 250 years. Since paraffin wax is itself flammable, the consequences of any gas combustion could be significant from the point of view of

flammability considerations. Strict controls are therefore advisable on the level of filling of each drum.

CONCLUSIONS

The conclusions of this assessment of radiolytic H_2 production are summarized as follows :

(i) The radiolytic production of H_2 from paraffin-wax-encapsulated waste is dominated by the radiation energy released from ^{60}Co.

(ii) The yields of H_2 from radiolysis of paraffin wax by gamma radiation are assumed, using n-hexadecane as a model; this model is reasonably close to a waxy paraffin, so confidence can be placed on the data, but definitive experimental data would be useful.

(iii) The energy deposition rate from alpha-radioactive wastes is a complex matter, largely dependent on the particle size of the emitting waste material. For the inventory used in this assessment, the impact of alpha-emitting isotopes is minimal; however, if any increase to the alpha inventory is anticipated then careful assessment of the impact of particle size should also be addressed.

(iv) The radiolytic production of H_2 will proceed at an initial rate equivalent to approximately $4.4\times10^2 cm^3 yr^{-1}$ in 200-litre drums that are partly filled with 120 litres of encapsulated waste. The gas production rate will fall to a value of $7.2 cm^3 yr^{-1}$ after 100 years, and a relatively constant value of $4.0\ cm^3 yr^{-1}$ after 200 years.

(v) The following safety implications attend this rate of H_2 production into the air space of each waste drum :

- the lower flammable limit for H_2 in air will be reached in about 25 years;
- the lower explosive limit for H_2 in air would not be reached in 1000 years;
- the drum will not become significantly pressurized (a 1.5 bar pressure vessel) in less than 1000 years.

(vi) The timescale in which these safety-related limits are reached is strongly dependent on the level of filling of each waste drum. A reduction of the air space inside each drum (say by 50%) would reduce the time required to reach the lower flammable limit to 6 years.

(vii) In the light of the above findings it is concluded that this method of waste encapsulation, with the given inventory, may be acceptable under the condition that strict controls are in place for the level of drum filling.

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